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(54) IMPROVED PROCESS FOR PREPARING HIGHLY FILLED
 ACRYLIC ARTICLES

(71) We, ROHM AND HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19015, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

This invention is concerned with highly filled acrylic articles and their preparation. The process enables the preparation of acrylic sheet having high flame retardancy, low smoke evolution, ease of handling and fabrication, high chemical and stain resistance, and of controlled thickness. Such sheet has a variety of applications, such as for surfacing material in bathroom, kitchen, and various indoor and outdoor architectural applications. Fillers are introduced into resins to impact cost reduction, reinforcement, flame retardancy, and marble-like appearance. For flame retardancy and cost reduction, high levels of filler are desirable. At low to moderate levels of filler, viscosity of the polymerisable resin composition is low and settling of the dense filler particles occurs rapidly. As the level of filler is increased, viscosity increases rapidly and the mixes become increasingly thixotropic with the result that filled resin pastes are difficult to handle and separation is still a problem. U.S. Patent 3,780,156 describes a process for decreasing the viscosity of a polymerisable mixture of a filled polymerisable polymer in monomer by the further addition of aliphatic monoacid viscosity modifiers.

According to this invention highly filled acrylic articles are made by moulding or casting a polymerisable resin composition which comprises:

(a) a solution of polymer in monomer in a ratio of 1:9 to 1:1 by weight polymer:monoethylenically unsaturated monomer wherein (i) said polymer comprises at least 50 percent by weight (C_1 to C_8)-alkyl methacrylate mers and 0.01 percent to 8 percent by weight copolymerisable ethylenically unsaturated carboxylic acid mers and has a molecular weight of 20,000 to 100,000; and (ii) said monomer comprises at least 50 percent by weight (C_1 to C_8)-alkyl methacrylate;

(b) a catalytic amount of polymerisation promoter system;

(c) 40 percent to 80 percent inert particulate filler, based on total blend weight. The invention also comprises the moulding or casting process for preparing highly filled acrylic articles, in particular acrylic sheet, by forming and curing the polymerisable resin composition.

The polymerisable compositions are conveniently made by forming solution (a), mixing it with component (b) and blending the resulting mixture with component (c).

The preferred mers of ethylenically unsaturated carboxylic acid in the polymer used in the resin compositions of the invention are methacrylic and/or acrylic acid mers. The balance (if any) of the polymer, apart from the C_1 to C_8 -alkyl methacrylate mers preferably comprises mers of one or more of the following:

(C_1 to C_8)-alkyl acrylates, styrene, alkyl styrenes, vinyl acetate, acrylonitrile, and methacrylonitrile. Preferably, the polymers used in this invention have a molecular weight of from 40,000 to 90,000; most preferably from 50,000 to 80,000. Surprisingly, the presence of the acid moiety in the thermoplastic polymer provides dispersions which are not highly thixotropic; the presence of small levels of acid in the acrylic polymer contributes to the combination of low viscosity and low settling performance of the filled casting mixture. It is believed that the polymer molecular weight and the level of acid in the acrylic polymer are

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interrelated although this inter-relationship is not fully understood. Accordingly, the benefits of this invention may, we believe, be achieved by adjusting the concentration of polymer in the polymer-in-monomer solution while maintaining a given level of acid in the polymer, or by adjusting the level of acid in the polymer while maintaining a given polymer concentration in the polymer-in-monomer solution, or by simultaneously adjusting both the polymer concentration in the polymer-in-monomer solution and the level of acid in the polymer.

The monomer of the polymer-in-monomer solution comprises at least 50 percent by weight (C_1 to C_8)-alkyl methacrylate, the balance (if any) comprising one or more of the following copolymerisable compounds:

(C_1 to C_8)-alkyl acrylate, styrene, alkyl styrenes, vinyl acetate, acrylonitrile, methacrylonitrile, methacrylic acid and acrylic acid and, optionally 0.01 to 1.0 percent, based on total polymerisable mixture of copolymerisable polyethylenically unsaturated monomer, preferably comprising one or more of the following: alkylene dimethacrylates, trimethacrylates, diacrylates, and triacrylates; divinyl benzene, triallyl cyanurate, and diallyl phthalate.

The inert particulate filler is preferably one or more of the following: hydrated alumina, calcium carbonate, clays, silicas, silicates, metal oxides, and magnesium oxychloride. More preferred inert fillers are hydrated alumina and calcium carbonate. Hydrated alumina is the most preferred.

The polymerisable mixture comprises 40 percent to 80 percent inert particulate filler based on total mixture. More preferably, the mixture comprises 50 to 70 percent inert filler, most preferably 60 percent to 67 percent inert filler.

The mixture may further comprise fibrous reinforcement; for example of inorganic fibers such as glass fibers, boron whiskers or graphite fibers; natural fibers such as jute, sisal, and bagasse; and synthetic organic fibers, such as nylon fibers. A preferred amount of fibrous material is up to 30 percent by weight of the total fiber-containing mixture.

The polymerisation promoter preferably contains free radical polymerisation catalyst which is present in the final mixture in an amount of 0.01 to 1.0 parts per hundred of the total mixture. This promoter system preferably also comprises, based on total polymerisable mixture, one or more of the following components 0.01 to 0.5 parts per hundred release agent, 0.01 to 0.5 parts per hundred wetting agent preferably nonionic and/or anionic surfactant, 0.01 to 1.0 parts per hundred ultraviolet absorber, and 0.001 to 0.01 parts per hundred polymerisation regulator. Suitable release agents include aliphatic monoacids and diacids (for example, Zelec UN), lecithin, sulfosuccinates (for example, Aerosol OT), and stearic acid. Particularly useful are ethoxylated alkyl phenols (for example, "Triton" X-100 an octyl phenol polyether alcohol having 9 to 10 ether groups. An especially useful UV absorber agent is hydroxyphenyl-substituted benzotriazole, available commercially as "Tinuvin" P. A useful polymerisation regulator is terpinolene (a monocyclic terpene). Preferably, the polymerisation promoter system comprises at least one peroxide polymerisation catalyst, for example *t*-butyl peroxy-pivalate, acetyl peroxide, and *t*-butyl peracetate (which are available commercially as "Lupersol" 11, APO -25, and Lupersol 70, respectively. The words "Triton", "Tinuvin" and "Lupersol" are Registered Trademarks.

The compositions can be cured and formed in or on any mold or casting surface. Preferably a closed cell apparatus, capped open cell apparatus, open-face mold, compression mold, injection mold or continuous-casting apparatus is used. Suitable closed cell apparatus includes apparatus used for sheet preparation in both conventional oven-casting operations and in vertical processes. Especially preferred is the closed cell cast polymerisation process, wherein the closed cells are made from glass. When closed cell cast polymerisation is practiced, preferably the polymerisable mixture is subjected to reduced pressure of about 25 to 30 psig to remove entrapped volatile gases prior to introducing it into the closed cell.

In practicing this invention, various techniques may be employed in order to achieve a variety of colours, patterns, and surface structures. A variety of decorations may be imparted to the finished sheet by incorporating into the polymerisable mixture components such as opacifiers, pigments, metallic flakes, unpigmented or pigmented concentrates based on isotactic poly(methyl methacrylate) for marbleizing or veining, and/or particulate matter such as white bar sand, red brick dust, and gray cinder dust, and gray cinder dust. An especially useful process for incorporating the isotactic poly(methyl methacrylate) concentrate mentioned above is described in U.S. Patent 3,050,785. Matte surfaces may be achieved by incorporating "flattening agents" into the mixture, by applying matte surface transfer film to the mold prior to filling or by abrasive post-treatment of the sheet. A satin finish may be obtained by post-heating the cured article, for example the sheet, at 120°C to 150°C for 0.1 to 0.25 hours. Embossed or structured surfaces may be achieved by applying suitable transfer paper or film to the mold prior to filling or by using molds having suitably

embossed or structured surfaces.

The invention is particularly useful in preparing filled acrylic sheet having a thickness of 0.1 to 4.0 inch, more especially 0.1 to 1.0 inch most especially, by closed cell cast polymerisation, 0.125 to 0.750 inch with a tolerance of plus or minus 0.020 inch to plus or minus 0.040 inch.

In a more preferred embodiment, the polymerisable composition comprises:

(a) 30 to 50 parts of polymer solution in monomer per hundred parts total mixture wherein the solution contains 10 to 50 percent by weight of polymer and wherein (i) said polymer comprises 80 to 99.9 percent by weight of any (C₁ to C₈)-alkyl methacrylate mers, 0.1 to 5.0 percent by weight of copolymerisable mono-ethylenically unsaturated carboxylic acid mers, the balance (if any) comprising (C₁ to C₈)-alkyl acrylate mers and wherein (ii) the monomer comprises (C₁ to C₈)-alkyl methacrylate;

(b) 0.01 to 1.0 parts per hundred parts total mixture polymerisation promoter system containing polymerisation initiator;

(c) 0.1 to 0.5 percent by weight based on total mixture of copolymerisable polyethylenically unsaturated compound;

(d) 50 to 70 parts inert filler per hundred parts total final mixture.

The final polymerisable mixture may suitably be subjected to a reduced pressure of about 25 to 30 psig to remove entrapped volatile gases after which it is preferably introduced into a closed cell; and cured at 50°C to 60°C for 3 to 5 hours, then at 130°C for 1 to 4 hours at a pressure of from atmospheric pressure to about 2000 p.s.i. and then cooled to 70°C to 80°C prior to parting the mold.

General preferred polymerisation conditions are a temperature of 20 to 130°C, a pressure from atmospheric to 2,000 p.s.i. for a time of 1 to 24 hours.

Sheet made by the process of this invention is very useful in bathrooms, kitchens, and various indoor and outdoor architectural applications. The preferred sheet-forming process is cell cast polymerisation, especially closed cell cast polymerisation. Further, the technology of foaming polymerisable, inert-filled acrylic compositions can be applied to the invention.

The combination of low mixture viscosity without filler settlement achievable by this invention allows for shorter and simpler mixing, easier processing and rapid polymerisation cycle time in the polymerisable mixtures.

Filled acrylic sheet of this invention can be conveniently installed using conventional procedures as surfacing applied to a backing such as, for example, asbestos-cement board to give panels which may be cut using variety saws, preferably equipped with carbide tipped blades, drilled, routed, scraped, sanded, filed, and polished. Filled acrylic sheet of greater thickness for example 0.250 to 1.0 inch, may be used without backing; sheet of this thickness is readily prepared by the process of this invention (as later exemplified in Example 27) by employing a mold having suitably selected release characteristics.

Some preferred embodiments are described, for the purpose of illustration only, in the following Examples in which all parts and percentages are by weight unless otherwise indicated and the following abbreviations are used: MMA = methyl methacrylate; pMMA = poly(methyl methacrylate); EA = ethyl acrylate; MAA = methacrylic acid; BMA = butyl methacrylate; BGDMA = 1,3-butylene glycol dimethacrylate. The commercially available agents used in the following examples are:

Zelec UN, an aliphatic monoacid; Tinuvin P, a hydroxyphenyl substituted benzotriazole; and Triton X-100, an ethoxylated alkyl phenol having an OPE number of 9-10. Some of the following Examples are for comparative purposes only.

Examples 1-9:

In order to establish the improvement of this invention, wherein the incorporation of copolymerisable ethylenically unsaturated carboxylic acid into the polymer provides unexpected and significant reduction in viscosity of the highly filled polymer in monomer solution and the casting mixture (said solution further including polymerisation promoter system) without settling of the filler, a series of filled solutions are prepared wherein the polymers are selected from the group of acid-containing (Examples 2, 3, 5, 7 and 9) and acid-free (Examples 1, 4, 6 and 8) polymers and copolymers and the viscosity of the filled solutions is measured and compared. Exemplary of these two types of polymers are the following:

Example 1:

An acid-free polymer prepared from the following monomer system:

5	Component	parts by weight	5
	MMA	97.93	
	<i>n</i> -dodecyl mercaptan	2.01	
	lauroyl peroxide	0.0398	
	acetyl peroxide	0.0465	
10	<i>t</i> -butyl peroxide	0.0070	10
	2.8% oxalic acid in H ₂ O	0.0025	

Example 2:

An acid-containing polymer prepared from the following monomer system:

15	Component	parts by weight	15
	MMA	95.92	
	MAA	2.01	
20	<i>n</i> -dodecyl mercaptan	2.01	20
	lauroyl peroxide	0.0398	
	acetyl peroxide	0.0465	
	<i>t</i> -butyl peroxide	0.0070	
	2.8% oxalic acid in H ₂ O	0.0025	

25 The solutions shown in Table 1 are prepared by dissolving the polymer in MMA in a
 30 polymer:monomer ratio of 25:75 parts by weight. Filler, selected from hydrated alumina
 ("Alcoa" (Registered Trademark) C-331 and Hydral 710; different particle size) and
 calcium carbonate (Camel White), is mixed into the solution in varying proportions as
 shown in Table 1. The resulting mixtures are blended, respectively, for three minutes using
 a high shear bench top stirrer. The temperature increases to 120°F during this operation.
 The mixtures are then cooled to 75°F and the viscosity is measured at 75°F at 2 rpm and at
 20 rpm using a Brookfield Model RVF Viscometer with a Number 4 Spindle. The results,
 presented in Table 1, show that the viscosity of casting mixtures prepared from
 35 acid-containing polymers is diminished by a factor of from 10 to 900 relative to the viscosity
 of casting mixture prepared from acid-free polymers.

TABLE I

Ex. No.	Solution (Monomer:Polymer = 75:25)	Filler ^a	Solution: Filler	Brookfield RVF Viscometer, Number 4 Spindle 2 rpm	Brookfield RVF Viscometer, 20 rpm
1 (Comparative)	MMA/p(MMA)	Alcoa C-331	35:65	90,000 cps	>10,000 cps
2	MMA/(MMA/MAA,2%) ^b	Alcoa C-331	35:65	500 cps	500 cps
3	MMA/(MMA/MAA,1%) ^b	Alcoa C-331	35:65	~100 cps	290 cps
4 (Comparative)	MMA/(MMA/EA,13%) ^b	Alcoa C-331	33:67	45,000 cps	>10,000 cps
5	MMA/(MMA/EA,12%/MAA,2%) ^b	Alcoa C-331	33:67	500 cps	650 cps
6 (Comparative)	MMA/(MMA/EA,13%) ^b	Hydral 710	50:50	94,000 cps	>10,000 cps
7	MMA/(MMA/EA,12%/MAA,2%) ^b	Hydral 710	50:50	1,250 cps	500 cps
8 (Comparative)	MMA/p(MMA)	Camel White	40:60	42,500 cps	9,600 cps
9	MMA/(MMA/MAA,2%) ^b	Camel White	40:60	250 cps	200 cps

^aAlcoa C-331 = hydrated alumina, particle size = 8.0 μ (microns)

Hydral 710 = hydrated alumina, particle size = 0.5 μ

Camel White = calcium carbonate, particle size = 2.0 μ

^bcp = copolymer

Examples 10-19:

Since previous laboratory experience with filled acrylic sheet has shown that testing mixtures based on formulations containing 60 percent to 70 percent by weight hydrated alumina and 0.2 percent to 0.4 percent by weight crosslinking monomer provided for desirable flammability, handleability and chemical and physical properties, a number of acrylic polymers are evaluated in polymer in monomer solution mixtures filled with 60 percent hydrated alumina (Alcoa C-331) and 0.2 percent BGDMA, based on total weight, to determine the optimal polymer in monomer concentration which imparts to the filled mixtures a desirable combination of flow characteristics and controlled settling properties. Filled mixtures are prepared for viscosity determination at 60 rpm and 6 rpm according to the following formulation: Alcoa C-331/polymer + MMA/BGDMA/Zelex UN/stearic acid/Triton X-100/Tinuvin P = 60.0/40.0/0.2/0.12/0.008/0.008/0.01. The data in Table II shows the viscosity and degree of "top clearing" (separation and settling of filler resulting in clearing of upper part of mixture) by which a prior art filled mixture, Example 10 containing an acid-free polymer, is characterized. The results in Table II further show that filled mixtures containing low molecular weight acid-free polymers, Examples 11-13, yield lower viscosity as compared with Example 10 results. However, the low viscosity of these mixtures is accompanied by settling of the filler, which results in the characteristic known in the field as "top clearing". Filled mixtures containing low molecular weight polymers prepared according to the invention, which polymers contain MAA, Examples 14-17, unexpectedly have been found to display the combination of low viscosity and minimal settling of filler and, particularly, low thixotropy. Addition of MAA to the relatively high molecular weight polymer used to give the filled mixture of Example 10 yielded mixtures, Examples 18 and 19, which display diminished viscosity accompanied, however, by undiminished filler settling. The optimal combination of low viscosity, low settling and low thixotropic properties was observed in the use of the polymer of Example 15.

TABLE II

Example No.	Polymer Composition	Molecular Weight	Viscosity (cps) at 60/6 rpm	vs. Polymer	Concentration	8.8%	14%	12.0%	14.0%
			4.0%	6.0%	8.0%	8.8%	14%	12.0%	14.0%
10 (Comp.)	MMA/EA 99/1	100,000	500/1900 (8/16)	1000/3500 (3-7)	2300/6800 (2)	3250/10400 (1-2)	-	-	-
11 (Comp.)	MMA/EA 96/4	59,000	-	170/<500 (9)	-	-	1430/3500 (2)	-	-
12 (Comp.)	MMA/EA 96/4	25,000	-	150/<500 (10)	-	-	860/900 (3)	-	-
13 (Comp.)	MMA/EA 55/45	60-70,000	-	320/800 (6)	480/1000 (4)	-	1250/1600 (2)	-	-
14	BMA/MMA/MAA 61.5/38.5/0.5	50,000	-	200/600 (6)	-	-	570/1200 (5)	-	-
15	MMA/EA/MAA 84.3/12.6/2.0	76,000	100/200 (2)	220/400 (2)	1060/1100 (0)	-	5200/4000 (0)	-	-
16	MMA/EA/MAA 84.3/12.6/2.0	45,000	50/<500 (3-4)	-	300/<500 (3)	-	1070/900 (0)	4100/2900 (0)	-
17	MMA/EA/MAA 83.2/12.3/2.0	20,000	20/100 (6)	-	90/100 (3)	-	300/240 (2)	540/500 (0)	1700/1200 (0)
18 (Comp.)	MMA/EA 99/1 +1% MAA	-	-	1000/3200 (3)	-	3000/8900 (2)	-	-	-
19 (Comp.)	MMA/EA 99/1 +2% MAA	-	-	960/2600 (3)	-	2650/7400 (2)	-	-	-

() = % top clearing in 24 hrs. at ambient temp.

Examples 20-30:

- A. The physical properties of filled acrylic sheets prepared by closed cell cast polymerisation followed by oven cure technique from casting mixtures having the formulations shown in Table III, wherein the polymer, in the initial polymer in monomer solution, is selected from a group having varying acid-free acid-containing compositions, are shown in Table III. Examples 23, 26 and 27 represent sheets prepared according to the invention; Examples 20-22, 24-25, and 28-30 represent comparison sheets. In these examples, the casting mixture is introduced, independently, to $14 \times 14 \times 0.125$ inch and $20 \times 28 \times 0.125$ inch tempered glass cell mold having poly(vinyl acetate) coated vinyl spacers and metal mold clips. The filled molds are placed directly into the ovens, and then cured at 60°C for 3 hours followed by 120°C for 2 hours. Upon cooling, the resultant sheets are isolated by separating the glass molds. The one difficulty observed in the use of acid-containing polymers in casting mixtures is increased mold adhesion, which causes "parting" problems, that is, difficulty in separating the product sheet from the glass mold. This difficulty is remedied by the incorporation of release agents in the casting mixture. The preparation of the sheet of Example 27 according to this invention is representative of the preparation of each of Examples 20-30 and is described in greater detail as follows:

TABLE III

Example No.	% Acrylic Polymer	Brookfield Viscosity (cps) 60 rpm	Brookfield Viscosity (cps) 6 rpm	% Residual Monomer	Flexural Strength		
					Stress (psi)	Modulus of Elasticity (psi $\times 10^6$)	Work (in. lbs.)
20 (Comparative)	8.8 MMA/EA 99/1 Comparison	3000	9600	-	8521	1.222	15.50
21 (Comparative)	6.0 MMA/EA 99/1 Comparison	850	3500	0.29	8427	1.212	16.76
22 (Comparative)	8.0 MMA/BA 55/45 Comparison	480	1000	0.19	6472	1.223	6.15
23 (Comparative)	10.0 BMA/MMA/MAA 64/61.5/38.5/0.5 Comparison	640	1700	0.21	6367	1.100	6.58
24 (Comparative)	6.0 MMA/EA 99/1 Comparison	810	2040	0.21	8338	1.229	11.12
25 (Comparative)	2.0 MMA/EA/MAA 83.2/12.3/2.0 Comparison	570	1400	0.23	6940	1.088	11.95
26	12.0 MMA/EA/MAA 83.2/12.3/2.0 Comparison	550	750	-	5597	1.156	6.39
27	6.8 MMA/EA/MAA 84.3/12.6/2.0 Comparison	302	575	0.21	8305	1.212	17.13
28 (Comparative)	10.9 MMA/EA 99/1 Comparison	5200	11,500	0.31	7940	1.218	25.59
29 (Comparative)	5.4 MMA/EA 99/1 Comparison	7300	18,000	0.33	6058	0.982	15.77
30 (Comparative)	3.2 Polyester Comparison	10000	20,000	0.35	5391	0.769	-

B. Example 27

A suitable mixing vessel is charged with 33.20 parts MMA monomer and the charge is stirred at about 20 to 30 rpm. Stearic acid, 0.20 parts, is dissolved in the stirred MMA monomer charge. This solution is charged with 6.80 parts polymer (MMA/EA/MAA = 84.3/12.6/2.0), 0.20 parts BGDMA, 0.12 parts Zelec UN, 0.01 parts Tinuvin P and 0.001 parts terpinolene, and the resulting solution is stirred vigorously (50-60 rpm) for about 0.1 to 1.0 hour. This solution is then further charged with 60 parts hydrated ammonium (Alcoa C-331) accompanied by vigorous stirring until the alumina is fully wetted; and the resulting mixture is further stirred vigorously for about 0.1 to 2 hours. This stirred mixture is still further charged with a polymerisation initiator mixture of 0.04 parts *t*-butyl peroxyphosphate and 0.02 parts *t*-butyl peracetate, and stirring is continued for about 0.1 to 0.5 hour to yield a casting mixture. This casting mixture is subjected to reduced pressure of about 25 to 30 psig for about 10 minutes and is then charged to a 20 × 28 × 0.125 glass cell mold. The sealed filled mold is placed into a forced air oven preheated to 60°C and heated at 60°C for 3 hours, heated at 120°C for an additional 2 hours and then finally slowly cooled (10°C - 60 minutes) to about 70°C to 80°C whereupon the mold is parted to isolate the product sheet.

Example 31:

A 72 × 96 × 0.125 inch filled acrylic sheet according to the invention is prepared by vertical process closed cell polymerisation followed by rapid 155 minute cycle cure as follows:

A suitable mixing vessel is charged with 33.20 parts MMA monomer and the charge is stirred at about 20 to 30 rpm; then this solution is charged with 6.80 parts polymer (MMA/EA/MAA = 84.3/12.6/2.0), 0.20 parts BGDMA, 0.20 parts stearic acid, 0.12 parts lecithin, 0.002 parts terpinolene and 0.1 parts Tinuvin P and the resulting mixture is stirred vigorously (50 to 60 rpm) for about 0.1 to 1.0 hour. This solution is further charged with 60.0 parts hydrated alumina (Alcoa C-331) accompanied by vigorous stirring until the alumina is fully wetted. The resulting mixture is further stirred vigorously for about 0.1 to 0.5 hour to effect uniform distribution. This mixture is still further charged with a polymerisation initiator mixture of 0.025 parts acetyl peroxide and 0.02 parts *t*-butyl peracetate and the resulting casting mixture is further stirred for about 0.1 to 0.5 hour. The casting mixture is then subjected to reduced pressure of about 25 to 30 psig for about 0.15 hour to remove entrapped volatile gases, and then charged to a 72 × 96 × 0.125 inch glass cell mold. The sealed mold is then subjected to a rapid 155 minute cycle cure wherein the mold is heated from 50°C up to 130°C under initial pressure of about 1,000 psi and then up to 2,000 psi and then down to atmospheric pressure and then allowed to cool to 80°C over a period of 155 minutes. The mold is then parted and the filled acrylic sheet product is isolated. The physical properties of this product sheet are shown in Table IV. This sheet also exhibits excellent resistance to stains (for example, crayon, liquid shoe polish, ink, lipstick, hair color, tea, coffee, liquor, household disinfectant and furniture polish (aerosol spray) and chemicals (naphtha, ethyl alcohol, amyl acetate, toluene, benzene, lacquer thinner, ethyl acetate, 3% aqueous hydrogen peroxide, 5% aqueous phenol, 6.6% aqueous urea, and concentrated Clorox).

TABLE IV

1) <i>Flammability Performance</i>				
5	a)	ASTM E-84 Tunnel Test ¹		
		Flame Spread Rating	70 (Class II)	5
		Smoke Density	20	
10	b)	ASTM E-162 Radiant Panel Test		
		Flame Index	15	
	c)	Oxygen Index	39	
10	d)	Smoke Density (R&H P-148D)		10
		Max. Density, %	1.0	
	e)	NBS Smoke Chamber		
		Max. Density	1-12	
	f)	Room Corner Test Performance ²	Excellent	
15	2)	<i>Specific Gravity</i>	1.698	15
	3)	<i>Rockwell Hardness</i>	M-80	
20	4)	<i>Izod Impact, notched (ft. lbs.)</i>	0.3	20
25	5)	<i>Tensile Properties (ASTM D-638-68, 0.2"/min.)</i>		
		Stress to Break (psi)	3,400	
25		Modulus of Elasticity (psi)	1,400,000	25
30	6)	<i>Flexural Properties (ASTM D-790-66, 0.1"/min.)</i>		
		Stress to Break (psi)	7,300	
30		Modulus of Elasticity (psi)	1,200,000	30
35	7)	<i>Deflection Temp. Under Load (ASTM D-648-61)</i>		
		264 psi, °F	212	35
		264 psi, °C	100	
40	8)	<i>Stain Resistance Tests for Sanitary Ware*</i>		
		ANSI Z124.1 (1974 Standard)	Passes	40
45		IAPMO (1972 Standard) -	Stains	
			Chemicals	Passes
			Cigarette	Passes
			Burn	Passes
	9)	<i>Water Absorption (ASTM D-570)</i>		
50		% Wt. Gain, 23°C,	24 Hours	
			7 days	50
			0.06	
			0.16	
55	¹ Laminated to asbestos/cement board			55
	² Two 8' × 8' walls, 8' × 8' ceiling panels on standard wallboard. Ignition source 6 lbs. plastic coated milk cartons in 32 gal. polyethylene trash can.			
60	* Contact with crayon, ink, liquid shoe polish, lipstick, hair coloring, iodine, mercur-ochrome, tea, coffee, beet juice, dyes, liquor, household disinfectant and furniture polish aerosol sprays, naphtha, ethyl alcohol, ethyl acetate, amyl acetate, toluene, benzene, lacquer thinner, acetone, concentrated Clorox, 3% aqueous hydrogen peroxide, 5% aqueous phenol, 6% aqueous urea, or 10% household ammonia produces no permanent defects on filled acrylic sheet.			60

WHAT WE CLAIM IS:

1. A highly filled acrylic polymeric article made by moulding or casting a polymerisable resin composition comprising:
 - (a) a solution of polymer in monomer in a ratio of 1:9 to 1:1 by weight polymer: monoethylenically unsaturated monomer wherein (i) said polymer comprises at least 50 percent by weight (C_1 to C_8)-alkyl methacrylate mers and 0.01 percent to 8 percent by weight copolymerisable ethylenically unsaturated carboxylic acid mers and has a molecular weight of 20,000 to 100,000; and (ii) said monomer comprises at least 50 percent by weight (C_1 to C_8)-alkyl methacrylate;
 - (b) mixed into said solution a catalyst amount of polymerisation promoter system;
 - (c) blended into the resulting mixture 40 percent to 80 percent inert particulate filler, based on total blend weight.
2. An article as claimed in Claim 1 wherein the copolymerisable ethylenically unsaturated carboxylic acid mers comprise methacrylic and/or acrylic acid mers.
3. An article as claimed in Claim 1 or Claim 2 wherein the polymer also contains mers of one or more of the following: (C_1 to C_8)-alkyl acrylate, styrene, alkyl styrenes, vinyl acetate, acrylonitrile, and methacrylonitrile.
4. An article as claimed in any preceding claim which further contains mers of one or more of the following monomers: (C_1 to C_8)-alkyl acrylates, styrene, alkyl styrenes, vinyl acetate, acrylonitrile, methacrylonitrile, methacrylic acid, and acrylic acid, alkylene diamethacrylates, tri-methacrylates, diacrylates, and triacrylates; divinyl benzene, triallyl cyanurate, and diallyl phthalate.
5. An article as claimed in any preceding claim wherein the polymerisation promoter comprises, based on total composition, 0.01 to 1 parts per hundred of free radical polymerisation catalyst.
6. An article as claimed in Claim 5 wherein the polymerisation promoter system further comprises one or more of the following components: release agent, wetting agent, UV absorber, and polymerisation regulator.
7. An article as claimed in any preceding claim wherein the inert filler comprises one or more of the fillers: hydrated alumina, calcium carbonate, clays, silicas, silicates, metal oxides, and magnesium oxychloride.
8. An article as claimed in any preceding claim which further contains opacifier, pigment, and/or decorative additive.
9. An article as claimed in any preceding claim which further contains up to 30 percent by weight (of total composition) of fibrous reinforcement.
10. An article as claimed in any of Claims 4 to 9 which contains 0.01 to 1 percent based on total composition of units of polyethylenically unsaturated monomer.
11. An article as claimed in Claim 1 which is made by moulding or casting a polymerisable resin composition comprising (a) 30 to 50 parts of polymer solution in monomer per hundred parts total composition wherein the solution contains 10 to 50 percent by weight of polymer and wherein (i) said polymer comprises 80 to 99.9 percent by weight of (C_1 to C_8)-alkyl methacrylate mers, 0.1 to 5.0 percent by weight copolymerisable monoethylenically unsaturated carboxylic acid mers the balance (if any) comprising (C_1 to C_8)-alkyl acrylate mers and (ii) the monomer comprises (C_1 to C_8)-alkyl methacrylate, (b) 0.01 to 1.0 parts per hundred parts total composition of polymerisation promoter system containing polymerisation initiator, (c) 0.1 to 0.5 percent by weight total composition of copolymerisable polyethylenically unsaturated compound, (d) 50 to 70 parts inert filler per hundred parts total composition.
12. An article as claimed in any preceding claim which is sheet having a thickness of 0.1 to 4.0 inch.
13. An article as claimed in any preceding claim which is sheet having a thickness of about 0.1 to 1.0 inch.
14. An article as claimed in Claim 1 made by moulding or casting a polymerisable resin composition substantially as described in any of the foregoing Examples 2, 3, 5, 7, 9, 14 to 17, 23, 26, 27 and 31.
15. A process for preparing a highly filled acrylic polymeric article as claimed in any preceding claim, which comprises moulding or casting the polymerisable resin composition.
16. A process as claimed in Claim 15 wherein the composition is moulded in a closed cell, capped open cell, open-face, compression, injection or continuous-casting type of mould.
17. A process as claimed in Claim 15 or 16 wherein the polymerisation is carried out by heating at a temperature of about 20°C to 130°C at a pressure of from atmospheric pressure to 2,000 psi for 1 to 24 hours.
18. A process as claimed in any of Claims 15 to 17 wherein, before moulding or casting, the mixture is subjected to a reduced pressure of 25 to 30 psig to remove entrapped volatile

gases and the subsequent polymerisation is carried out at 50°C to 60°C for 3 to 5 hours, then at 130°C for 1 to 4 hours at a pressure of from atmospheric pressure to about 2,000 psi followed by cooling to 70°C to 80°C prior to removing the article.

19. A process as claimed in claim 15 substantially as described in any of the foregoing Examples 23, 26 and 31.

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